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Title: Method for Centrifuging a Slurry Containing Terephthalic Acid Crystals

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(54) Title of the Invention: **Method for Centrifuging a Slurry Containing Terephthalic Acid Crystals**

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SPECIFICATION

1. Title of the Invention

Method for Centrifuging a Slurry Containing Terephthalic Acid Crystals

2. Claims

1. A method for centrifuging a slurry containing terephthalic acid crystals by means of repeating a procedure whereby a slurry containing terephthalic acid crystals is filtered using a batch-type centrifuge to separate the mother liquor, and the resulting terephthalic acid cake is scraped off, said centrifugation method being characterized in that the thickness of the scraping residue is gradually reduced.

2. The centrifugation method according to claim 1, wherein acetic acid is sprinkled onto the terephthalic acid cake prior to scraping, and the sprinkled acetic acid is removed from the cake as a result of centrifugation.

3. The centrifugation method according to claim 1 or claim 2, wherein, when the thickness of the scraping residue is reduced, each reduction in thickness is greater than the previous reduction in thickness.

4. The centrifugation method according to claim 1, 2 or 3, wherein the slurry containing terephthalic acid crystals is the reaction solution obtained as a result of the oxidation of p-xylene with oxygen-containing gas in an acetic acid solvent in the presence of a heavy metal catalyst.

3. Detailed Description of the Invention

The present invention relates to a method for obtaining terephthalic acid crystals by means of centrifuging a slurry containing terephthalic acid.

Polyester fibers have been produced from dimethylterephthalate and ethylene glycol in the past, but the so-called direct polymerization method from terephthalic acid and ethylene glycol has been used in recent years because the cost of the final product is lower. High-purity terephthalic acid capable of direct polymerization is obtained by means of subjecting the resulting crude terephthalic acid to purification or another type of aftertreatment. However, purification or other type of aftertreatment is costly because of the complexity of the process and other factors, and the cost of the terephthalic acid itself is increased, so the advantages of using the direct method are ultimately reduced. Research is being performed regarding methods for producing high-purity terephthalic acid with which terephthalic acid suitable for direct polymerization can be obtained merely as a result of the oxidation of p-xylene and the solid-liquid separation of the product without performing purification or another aftertreatment.

When high-purity terephthalic acid capable of being used for direct polymerization is produced without performing purification or another aftertreatment, the terephthalic acid obtained as a result of solid-liquid separation contains metals because heavy metal catalysts are used for p-xylene oxidation and because the equipment corrodes. It is necessary separate the terephthalic acid slurry into solid and liquid fractions once the conventional reaction is completed, and then further to repeat two or three times the procedure in which the product is reslurried and separated again into solid and liquid fractions. Repeating the solid-liquid separation and reslurrying several times complicates the equipment, increases equipment costs, and results in a complex and inefficient procedure.

Methods for separating a parent liquor and crystals by means of centrifuging a slurry include batch centrifugation methods, which involve repeating a procedure whereby a slurry is fed to the basket of a centrifuge, the mother liquor is separated by means of centrifugal force, the product is washed with a solvent, and the cake deposited on the inside walls of the basket is scraped off with a knife blade; and continuous centrifugation methods that involve simultaneously recovering the mother liquor and the cake while continuously feeding the slurry to a centrifuge. The present invention is appropriate for the batch centrifugation methods and provides a process whereby the metal content of the resulting terephthalic acid can be stabilized at as low a level as possible without repeating the process whereby a slurry is separated into solid and liquid fractions and the product is reslurried numerous times.

In batch centrifugation, a procedure whereby the cake deposited on the inside walls of the basket is scraped off using a knife blade is repeated. Taking into consideration the lateral vibration in the radial direction of the centrifuge basket, it is not possible to scrape off all of the cake with a knife blade. Some cake is usually left on the filter (this remaining cake is called a heel) in order to prevent the filter on the inside walls of the basket from being damaged by the knife blade, and is transferred to the next slurry feed step.

The remaining cake filters the terephthalic acid slurry during the solid-liquid separation of the terephthalic acid. Therefore, the remaining cake protects the filter and has the effect of reducing leakage of terephthalic acid particles. However, centrifuging the terephthalic acid crystals by means of repeating this process causes the filtration resistance of the heel to change

over time and the rate of removal of the slurry mother liquor to gradually decline. Therefore, when the liquor becomes more difficult to remove, the heel is washed with an alkali and duplicated[1]. A method whereby the heel thickness is periodically changed when a slurry of terephthalic acid crystals is centrifuged and the terephthalic acid cake is scraped off has been proposed in order to prolong the period of washing the heel with an alkali. When this method is used, it is possible to prolong the time until the parent liquor becomes difficult to remove, and the alkali washing period can last for two to four hours, or 60 cycles. However, a fairly large metal content remains in the terephthalic acid, and the metal content is too high and fluctuates widely when reslurrying and solid-liquid separation are performed just once,[2] making it completely impossible to use the product as a terephthalic acid for direct polymerization. It is also possible to reduce the metal content of the terephthalic acid by means of reducing the period of alkali washing. However, this approach is impractical because of a reduction in the capacity of the centrifugal separator. Moreover, there is a disadvantage in that the metal content of the terephthalic acid is raised as a result of the alkali used for alkali washing.

The inventors discovered the following as a result of performing intense studies of methods for obtaining high-purity terephthalic acid suitable for direct polymerization in which the metals contained in the reaction system as a result of equipment corrosion and the use of heavy metal catalysts in the oxidation of p-xylene are removed as a result of performing a single cycle of reslurrying and solid-liquid separation[3]. That is, it became clear that the amount of metal that is held inside the terephthalic acid particles differs somewhat with the concentration of catalyst used in the reaction, but is always very small, and that most of the metal content of the terephthalic acid comes from two sources: the metal-containing liquid that remains in the terephthalic acid, and the metal adsorbed on the topmost layer of the terephthalic acid.

In other words, it became clear that removing all of the metal-containing liquid and removing as much as possible the metal component adsorbed on the cake surface are of the utmost importance to reducing the metal content of the terephthalic acid by means of solid-liquid separation.

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[1] Corrected as indicated in item 6(1) of the Procedural Correction on the last page of the Japanese original.
[2] Corrected as indicated in item 6(2) of the Procedural Correction on the last page of the Japanese original.
[3] Corrected as indicated in item 6(3) of the Procedural Correction on the last page of the Japanese original.

From 3 to 10% of parent liquor always remains on the cake in centrifuges in which the cake cannot be rinsed with acetic acid, that is, in which it is impossible to add acetic acid to the separated solid cake and to make the cake into a slurry[4]. The metal content of the mother liquor is 0.1 to 1%; therefore, it is not possible to reduce the metal content of terephthalic acid to several parts per million by means of a simple solid-liquid separation.

The method, as disclosed in JP (Kokai) 52-133940, in which acetic acid that has been sufficiently heated is sprinkled onto a cake obtained as a result of solid-liquid separation is an example of a method whereby as much of the metal content adsorbed on the cake surface as possible is removed. Nevertheless, it cannot necessarily be said that the effect of even this method is sufficient unless the mother liquor of the reaction is thoroughly removed from the cake.

An object of the present invention is to completely remove the liquid with a metal content from the terephthalic acid cake by means of preventing changes over time in the filtration resistance of the heel.

This object can be accomplished with the help of a method for centrifuging a slurry containing terephthalic acid crystals as a result of repeating a procedure whereby a slurry containing terephthalic acid crystals is filtered using a batch-type centrifuge to separate the mother liquor, and the resulting terephthalic acid cake is scraped off, with the thickness of the scraping residue gradually being reduced. It is also possible to remove even more of the metal content from the terephthalic acid as a result of sprinkling acetic acid onto the cake prior to scraping, and then removing the sprinkled acetic acid from the cake by way of the centrifugation. Moreover, the filtration resistance of the heel can be further stabilized and a terephthalic acid of constant purity can be obtained as a result of making the extent to which the thickness of the scraping residue is reduced each time greater than the extent to which it was reduced the preceding time. The present invention will now be described in further detail.

The method of the present invention is performed by means of varying the thickness of the small amount of cake (heel) remaining on the filter in a process in which a slurry of terephthalic acid is subjected to solid-liquid separation using a batch-type centrifuge, preferably

[4] Corrected as indicated in item 6(4) of the Procedural Correction on the last page of the Japanese original.

a batch-type centrifuge capable of acetic acid rinsing. The thickness of this heel is usually from 3 to 15 mm in the case of terephthalic acid. Filtration performance improves with a thinner heel, and filtration performance quickly deteriorates with a thicker heel. Moreover, filtration performance rapidly deteriorates when heel thickness is kept constant. For instance, when centrifugation is performed at the same heel thickness, filtration performance starts to deteriorate with 20 cycles, and solid-liquid separation becomes impossible with 60 cycles. Consequently, it is preferred in the present invention that the heel thickness be changed so that a new heel surface is used every 20 cycles. The metal content of the terephthalic acid increases if the heel thickness is greater than the heel thickness of the previous cycle. Consequently, good filtration performance can be realized wit the help of a method whereby the thickness of the heel gradually becomes smaller. Keeping the thickness of the newly formed heel at a low level from the start will yield very good initial filtration performance but will cause the heel thickness to decrease rapidly, and will reduce the total number of cycles from start to finish to just a few cycles. Therefore, it is preferred that the initial heel thickness be as large as possible. The heel should be thicker than the conventional 15 mm thickness, and 18 mm to 25 mm is preferred. If the heel is too thick, there will be a reduction in the amount of terephthalic acid that is scraped off per cycle, and the centrifuge will have a lower capacity. Moreover, a newly formed heel will have good filtration performance in the beginning; therefore, the method whereby the number of cycles is increased has been considered. However, filtration performance deteriorates with a thinner heel, reducing the total number of cycles from start to finish.

Ultimately, it is preferred that the thickness of the heel be reduced at specific intervals in order to always maintain good filtration performance and to prolong the time during which filtration performance remains good. It is preferred that the extent of thickness reduction be initially small and increase gradually, as described above. The cake thickness can be continuously reduced using mechanical means. It is also possible to vary the thickness automatically or manually with the aid of a machine in 5 to 15 steps.

When an acetic acid rinse is used, the amount of acetic acid is usually half to four times the amount of terephthalic acid in the cake.

When conventional methods are used, there are large variations in the metal content of the resulting terephthalic acid, and it eventually becomes difficult to complete solid-liquid separation in 60 cycles or more. However, the metal content of the terephthalic acid can be reduced and stabilized in 120 cycles as a result of the present invention. Moreover, a conventional basket is rinsed with an alkali every two to four hours, and the metal content in the separated terephthalic acid is high. However, acetic acid rinsing can prolong alkali washing to between 6 and 10 hours and to make it possible to obtain terephthalic acid whose metal content is sufficiently low to allow the acid to be used for direct polymerization.

The method of the present invention can be used for acetic acid slurries of terephthalic acid that are obtained as a result of the liquid-phase air oxidation of p-xylene in an acetic acid solvent using a heavy metal or bromine compound as the catalyst. With this objective in view, the method of the present invention is effective for the solid-liquid separation of high-purity terephthalic acid.

The present invention will now be described with working examples.

Working Example 1

First, 280 kg of acetic acid slurry (metal concentration of 0.5%) containing 30% of terephthalic acid (terephthalic acid center particle diameter of 150 μ) were fed for 40 seconds to an automatic batch centrifuge, parent liquor was sprinkled after 40 seconds of centrifugation, the product was washed with 120 kg of acetic acid (1.5 times the amount of terephthalic acid) that was kept at 105°C and contained 3% of water, the liquid was again sprinkled for 50 seconds, and the cake was scraped off five seconds later. The procedure was repeated. This method was initially performed so that the heel would be scraped off to a thickness of 18 mm. When the number of cycles and the heel thickness were gradually reduced and the extent of thickness reduction was gradually increased, the metal content stabilized at 2 ppm, as shown in Table 1. Alkali washing was performed after 120 cycles, and the procedure was repeated from the first cycle. As a result, the metal content of the terephthalic acid was constantly stable.

Table 1

Number of cycles	1–20	21–40	41–60	61–80	81–100	101-120
Heel thickness (mm)	18	17	15	12	8	3
Metal content (ppm)	2	2	2	2	2	2

Comparative Example 1

Table 2 shows the results of performing the same procedure as described in Working Example 1, with the exception that the heel thickness was not changed. The metal content also increased with 40 cycles or more, and solid-liquid separation became impossible with more than 60 cycles. Alkali washing was performed and the procedure was repeated from the first cycle, causing the metal content of the terephthalic acid to vary and more metal to be contained in the product.

Table 2

Number of cycles	1–20	21–40	41–60
Heel thickness (mm)	10	10	10
Metal content (ppm)	2	2 → 20	20 → 100

Working Example 2

Although initially adequate, the metal content gradually increased as a result of performing the same procedure as described in Working Example 1, with the exception that the heel thickness was reduced with the same intervals, as shown in Table 3. Alkali washing was performed after 120 cycles and the procedure was repeated from the first cycle, but the metal content increased before alkali rinsing.

Table 3

Number of cycles	1–20	21–40	41–60	61–80	81–100	101-120
Heel thickness (mm)	18	15	12	9	6	3
Metal content (ppm)	2	2	2	2	2→7	7→15

Comparative Example 2

The results in Table 4 were obtained when the same procedure as described in Working Example 1 was performed, with the exception that the heel thickness was periodically changed. The metal content was high.

Table 4

Number of cycles	1–20	21–40	41–60	61–80	81–100	101–120	121–140	141–160	161–180
Heel thickness (mm)	18	15	18	15	18	9	15	9	15
Metal content (ppm)	2	2	2 → 10	5 → 10	10 → 50	10 → 20	20 → 80	20 → 80	100 or more

Procedural Correction (Voluntary)

Date: December 17, 1978

Commissioner, Patent Office

1. Case No. 53-105740
2. Title of the Invention

   Method for Centrifuging a Slurry Containing Terephthalic Acid Crystals
3. Party Making the Amendment

   Relation to the Case: Applicant

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5. Sections Amended

   Detailed Description of the Invention of the Specification
6. Amendment Details

   (1) The "duplicated" on line 27 of page 3 of the translation is corrected to read, "recovered."

   (2) The "reslurrying and solid-liquid separation are performed just once" on line 6 of page 4 of the translation is corrected to read, "solid-liquid separation is performed just once."

   (3) The "a single cycle of reslurrying and solid-liquid separation" on line 16 of page 4 of the translation is corrected to read, "a single cycle of solid-liquid separation."

   (4) The "to make the cake into a slurry" on line 27 of page 4 of the translation is corrected to read, "to wash the cake."